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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Gasoline Fuel

We, ATLANTIC RICHFIELD COMPANY, a Corporation organized under the laws of the State of Pennsylvania, United States of America, of 260 South Broad Street, Philadelphia 1, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a motor fuel composition boiling in the gasoline boiling range and having high anti-knock characteristics and superior carburetor anti-icing properties. More particularly, this invention relates to a motor fuel boiling in the gasoline range containing tertiary butyl alcohol and a corrosion inhibitor.

In a more specific embodiment this invention relates to a motor fuel containing a combination of tertiary butyl alcohol, a corrosion inhibitor and a carburetor detergent compound.

For many years tetraethyl lead has been added to motor fuels in order to provide the improvement in anti-knock characteristics necessary to meet the high performance requirements of the modern automobile engines. The use of tetraethyl lead, however, gives rise to several problems. One of the problems is the cost of this component and, because of this, refiners have continually searched for cheaper compounds or means of providing the required octane characteristics of the motor fuel and thus reduce the amount of tetraethyl lead in their gasolines.

Another problem is that tetraethyl lead in gasoline produces harmful deposits in internal combustion engines which requires the addition to the gasoline of various types of scavengers and deposit modifiers to counteract the effect of the deposits. In addition, because of the toxicity of tetraethyl lead the amount which can be employed in gasoline has been limited for many years, but for the past several years there has been a gradually increasing pressure from Public Health authorities to reduce or eliminate entirely the lead content of gasoline because of its toxic effects.

There are additional problems which are associated with modern automotive engines. One of these is carburetor icing which causes stalling of the engine in cool, humid weather, particularly when the engine is cold. Another is the formation of dirt deposits in the carburetor barrel around the throttle plate area and on the throttle plate which prevents the plate from closing properly. These deposits are caused by dirt from the air, by "blow-by" from the engine itself and from exhaust fumes of other automobiles.

There is therefore a need for a motor fuel having high anti-knock characteristics, superior carburetor anti-icing properties and low corrosiveness for the metal parts of the fuel system of an internal combustion engine and preferably one having carburetor detergency properties.

It has been found that tertiary butyl alcohol (2-methyl-2-propanol) when added to motor fuel not only improves the anti-knock characteristics of the fuel but in addition it greatly alleviates, or in some instances completely eliminates, the carburetor icing problem. Thus the addition of tertiary butyl alcohol gives a two-way improvement to the gasoline, i.e. it improves both the anti-knock characteristics and the anti-icing properties of the gasoline.

The addition of tertiary butyl alcohol to gasoline however, is not free of disadvantages. The alcohol causes the gasoline to pick up water, for example, from refinery tank bottoms or from the product distribution system. This solubilizing effect of the tertiary butyl alcohol causes the fuel to carry a considerably higher water content than is normally found in gasoline. The most serious problem associated with water is that of corrosion of fuel system parts, particularly those made of steel, zinc or magnesium.

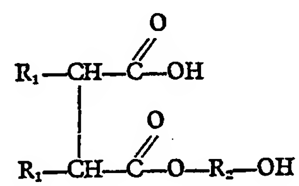
It now has been found that the corrosion characteristics of a motor fuel containing ter-

tiary butyl alcohol can be reduced to a minimum by the use of certain specific corrosion inhibitors in combination with the tertiary butyl alcohol. In addition it has been found that certain specific carburetors detergents can be added to the fuel containing the tertiary butyl alcohol and the corrosion inhibitor to provide a fuel which not only prevents deposits from forming in a clean carburetor, but also removes any deposits previously in the carburetor.

In accordance with this invention a motor fuel base boiling in the gasoline range which may contain tetraethyl lead is provided with additional anti-knock properties and superior carburetor anti-icing properties by the addition thereto of from 1 to 20 volume per cent based on the total volume of the fuel of tertiary butyl alcohol, preferably from 3 to 15 volume per cent. In order to reduce to a minimum the corrosiveness of the fuel for the metal parts of the fuel system of an internal combustion system there also is incorporated into the fuel from 20 parts per million (ppm) by weight to 100 parts per million (ppm) by weight based on the total weight of the fuel of a corrosion inhibitor which is a derivative of alkenyl succinic anhydride.

The motor fuel base component may be either the so-called "Regular Grade" gasoline base component or "Premium Grade" gasoline base component. The gasoline component may contain up to 3 cc's of tetraethyl lead per gallon of gasoline, or equivalent amounts of other lead additives such as tetra-methyl lead, however, the base gasoline component need not contain any tetraethyl lead, if it is of the type wherein the high anti-knock characteristics are provided by certain high octane hydrocarbon components. In addition the base gasoline may contain any of the various phosphate ester additives such as tri-cresyl phosphate. Moreover, in a particularly preferred embodiment of the invention the tertiary butyl alcohol is utilized to provide at least a portion of the high anti-knock characteristics to the gasoline thereby reducing the quantity of tetraethyl lead required to give the desired octane rating to the fuel.

As has been stated, the fuel containing the tertiary butyl alcohol tends to solubilize water and thus becomes corrosive. The corrosiveness of this fuel toward fuel system parts of an internal combustion engine can be reduced to a minimum by the use of a corrosion inhibitor particularly derivatives of alkenyl succinic anhydride. Compounds which have been found to be particularly suitable as corrosion inhibitors in accordance with this invention have the formulae (identified by Roman numerals and letters),

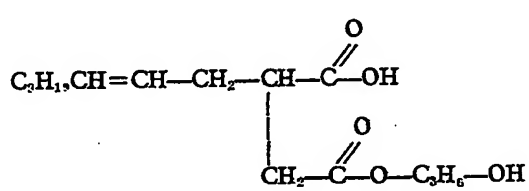


(I)

wherein one R_1 is an alkenyl radical having one double bond and from 8 to 16 carbon atoms with the other R_1 being hydrogen, and R_2 is a radical having the formula

$$—C_nH_{2n}—$$

with n being 2, 3 or 4. These compounds may be termed the monoester of an alkylene glycol with an alkenyl succinic acid. In a particularly preferred embodiment R_1 which is alkenyl is dodecenyl (12 carbon atoms) and R_2 contains 3 carbon atoms, for example



(Ia)

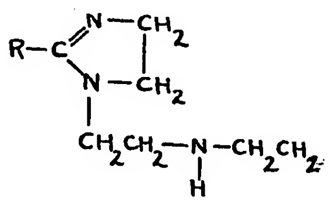
Compound (Ia) may be termed the monoester of propylene glycol with dodecenyl succinic acid. Obviously the isomeric compounds such as those wherein R_1 is branched chain also are equivalent to (Ia). Thus, the R_1 (when alkenyl) may range from octenyl to hexadecenyl and the corresponding alkenyl succinic anhydride may be monoesterified with ethylene glycol, propylene glycol or butylene glycol to give the corresponding mono ester of the succinic acid. Many of these compounds are available commercially.

In addition to the tertiary butyl alcohol and the corrosion inhibitor which have been described, a carburetor detergent also may be incorporated in the base gasoline. It has been found that certain compounds which function as carburetor detergents can be used in com-

bination with the corrosion inhibitor component of the gasoline. In general these compounds are derivatives of N-beta-hydroxyethyl ethylene diamine, i.e. derivatives of the structure

$$-\overset{|}{N}-CH_2CH_2-\overset{|}{N}-CH_2CH_2OH. \quad (II)$$

A particularly preferred compound has the formula



In this compound (II) the nitrogen atom of the ethylene diamine other than the nitrogen atom to which the beta-hydroxy-ethyl group is attached, forms a part of an imidazoline nucleus. The R of (III) may be an alkyl radical having from 12 to 20 carbon atoms or an alkenyl radical with one double bond and from 12 to 20 carbon atoms. Preferably the R is an alkenyl radical having 18 carbon atoms. Thus, if R is saturated, it may range from dodecyl to eicosyl, or if unsaturated, it may range from dodecenyl to eicosenyl. In the preferred compound, R is octadecenyl.

It has been found that the corrosion inhibitor, compound (I) or (Ia), and the carburetor detergent, compound (II), when employed in stoichiometric proportions form a salt which in turn may be employed as the combined corrosion inhibitor and carburetor detergent. In general about 2 parts by weight of compound (III) and one part by weight of compound (I) can be used to form the salt although an excess of compound (III) may be employed, e.g. 5 parts by weight of compound (III) to one part by weight of compound (I). In general from 20 ppm by weight to 100 ppm by weight, preferably 50 ppm by weight to 75 ppm by weight of the salt of compound (I) and compound (III) provide the necessary corrosion inhibition and carburetor detergency. Other derivatives of the N-beta-hydroxyethyl ethylene diamine, formula (II) also may be employed as the carburetor detergent, for example, the condensation product of methyl oleate with N-beta-hydroxyethyl ethylene diamine. This condensation reaction produces two isomeric amides. One of these is:

$$R-\overset{O}{\overset{/\!/}{C}}-\overset{H}{\overset{|}{N}}-CH_2CH_2-\overset{H}{\overset{|}{N}}-CH_2CH_2OH \qquad (IV)$$

and the other is:

$$H_2N-CH_2CH_2-\underset{}{\overset{\overset{R}{|}}{\overset{C=O}{\overset{|}{N}}}}-CH_2CH_2OH \qquad (IVa)$$

Compound (IV) generally predominates. The R group, when methyloleate is employed in the condensation, is of course, an alkenyl group having 17 carbon atoms. Other esters, for example, methyl stearate, wherein the R group is alkyl having 17 carbon atoms also may be employed. The R group may contain from 15 to 19 carbon atoms. The amides may be formed from the corresponding methyl ester and beta-hydroxyethyl ethylene diamine. These compounds are also commercially available.

Other compounds are well known as corrosion inhibitors in gasoline, however, they have been found to be ineffective for inhibiting corrosion of base gasoline containing tertiary butyl alcohol. Similarly, other carburetor detergents which have been employed in base gasolines have not been found to be compatible with the other components of the gasoline of this invention.

The following examples are provided to describe and illustrate the invention in more detail.

Example I

A number of runs were carried out to determine the effect of tertiary butyl alcohol on the octane performance of gasolines. In these studies the research octane number was determined in accordance with ASTM Method D-908 and the motor method octane number was determined in accordance with ASTM Method D-357. In addition road octanes were determined in accordance with the modified Uniontown Road Octane Method, a 5-car average being used.

When tested in commercial gasolines it was found that tertiary butyl alcohol had blending values of about 112 research octane number and 103 motor octane number. In making these

determinations 5 Premium commercial gasolines (representing a range of lead levels) and 6 Regular commercial gasolines (representing a range of lead levels), were used. Triplicate runs were made with each of these gasolines at two different levels of tertiary butyl alcohol. The tetraethyl lead savings in these fuels through the use of 5 per cent by volume and 10 per cent by volume of tertiary butyl alcohol are shown in Table I, the table showing the average for the Regular and for the Premium for each set of runs.

TABLE I

Fuel	*TBA	Allowable TEL reduction, ml/gal Research Method (avg.)	Motor Method (avg.)
Premiums	5	0.53	0.46
	10	0.85	0.82
Regulars	5	0.45	0.35
	10	0.70	0.69

*TBA = tertiary butyl alcohol

Allowable TEL reduction refers to the amount of TEL equivalent to the TBA. Thus, for a premium gasoline, if 5 per cent TBA is added, the amount of TEL could be reduced 0.53 ml per gallon and still maintain the same octane number as measured by the Research Method.

It was found when 10 per cent by volume of tertiary butyl alcohol was added to an unleaded high octane gasoline that the tertiary butyl alcohol was approximately equivalent to 10 volume per cent toluene in octane blend quality as shown in Table II.

TABLE II

Fuel	Research Octane No.	Motor Octane No.
Unleaded Base	100.0	91.5
Base+10% Toluene	101.3	91.7
Base+10% TBA	101.1	91.9

A commercial type gasoline was tested with 0 per cent, 5 per cent and 10 per cent by volume tertiary butyl alcohol with the tetraethyl lead level adjusted in the three fuels to give approximately the same laboratory octane numbers. The road octane of these fuels was then determined utilizing the modified Uniontown Road Octane Method (5-car average) as shown in Table III.

TABLE III

Test Fuel	Octane-Ratings Research	Motor	Road
Commercial Base+2.4 ml TEL/gal.	99.2	92.1	97.8
Base+5% TBA+2.0 ml TEL/gal.	99.5	92.1	97.5
Base+10% TBA+1.7 ml. TEL/gal.	99.4	92.0	97.7

These results show that fuels containing tertiary butyl alcohol perform on the road in accordance with the laboratory octane levels. The results of the octane performance of tertiary butyl alcohol in gasoline show that it can be utilized to replace all or a part of the tetraethyl lead in commercial grade gasolines.

Example II

In order to demonstrate the superior carburetor anti-icing properties of tertiary butyl alcohol in gasoline a standard chassis dynamometer icing test was utilized. In this test any make car in good mechanical condition may be utilized on a chassis dynamometer which is contained in a room maintained at a temperature of 40° ± 2°F. The air introduced into the carburetor is also at 40° ± 2°F. and has a relative humidity of 95 to 100 per cent. The car is subjected to the following steps:

1) The car is cooled until it reaches equilibrium with the temperature in the room
2) The car is then started and run at 1800 RPM (approximately 35—40 miles per hour) for 30 seconds under no load, i.e. only the inertial loal of the dynamometer rolls themselves
3) The car is braked to a stop and idled for 15 seconds
4) The car is accelerated to 1800 RPM and run for 30 seconds
5) Steps 3 and 4 are repeated. If the car stalls during idle it is restarted and the cycles are continued. At least 12 complete cycles (steps) and 4) are run. The test is stopped when 3 consecutive no-stall cycles have occurred or when 20 stalls have occurred.

The procedure which has been outlined was utilized for testing the carburetor anti-icing properties of tertiary butyl alcohol in gasoline.

Two base commercial fuels were evaluated without additive and with isopropanol or various amounts of tertiary butyl alcohol in a random sequence. The fuels were of different volatilities, the first being one wherein 56 per cent of the fuel evaporated at 212F. and the second being one wherein 60 per cent of the fuel evaporated at 212°F. A 1963 "Ford" Station Wagon was utilized as the test car. The results obtained are set forth in Table IV. The word "Ford" is a Registered Trade Mark.

TABLE IV

Test Fuel #1: 60% evap. at 212°F.

Fuel	Total Stalls/Test	Average Stalls
Base fuel	14, 12, 10, 11	11.75
Base fuel+1 1/2 volume per cent isopropyl alcohol	1, 1, 0, 1	0.75
Base fuel+2 volume per cent tertiary butyl alcohol	2, 6, 3	3.7
Base fuel+4 volume per cent tertiary butyl alcohol	2, 2, 2, 6, 2, 1, 1	2.3
Base fuel+5 volume per cent tertiary butyl alcohol	1, 0, 0, 0	0.25
Base fuel+6 volume per cent tertiary butyl alcohol	0, 0, 0, 0	0
Base fuel+0.01 volume per cent commercial surfactant de-icer	4, 5	4.5
Test Fuel #2: 56% evap. at 212°F.		
Base fuel	6, 12, 8, 7	8.3
Base fuel+1 1/2 vol. per cent isopropyl alcohol	0, 0, 0, 0	0
Base fuel+2 volume per cent tertiary butyl alcohol	0, 2, 3, 5	2.5
Base fuel+5 volume per cent tertiary butyl alcohol	0, 0, 0, 0	0
Base fuel+0.01 volume per cent commercial surfactant de-icer	4, 5, 4	4.3

These data demonstrate that with a highly volatile fuel 5 volume per cent of tertiary butyl alcohol when incorporated into such fuel substantially completely eliminates carburetor icing problems and, in fact, is better than the same fuel with 1 1/2 volume per cent isopropyl alcohol which is used commercially. With a fuel of lower volatility the 5 volume per cent is equivalent to 1 1/2 volume per cent tertiary butyl alcohol and eliminates carburetor icing completely.

EXAMPLE III

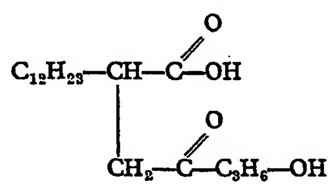
In order to demonstrate the effectiveness of a corrosion inhibitor of the present invention in a fuel containing tertiary butyl alcohol, in the presence of water several corrosion tests were carried out. In these tests 750 ml of the test gasoline and 0.75 ml of distilled water were placed in a one-quart jar and the two components stirred for one minute. A freshly sand blasted magnesium metal coupon (1" x 1") was suspended in the gasoline and the jar was stoppered. The jar was allowed to stand at room temperature undisturbed except for stirring for one minute twice each week. At the end of 30 days the test specimen was removed, dried and weighed. The increase in weight measured in milligrams gives the measure of the amount of corrosion. The base gasoline employed was a Premium grade gasoline base containing 3 ml per gallon of tetraethyl lead.

TABLE V

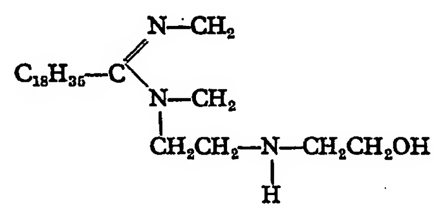
Gasoline Composition	Inhibitor, ppm by weight	Weight Gain, milligrams
Base gasoline	None	23.8, 22.5
Base gasoline+4 vol. %TBA[1]	None	29.1, 28.8
		25.9, 25.8
Base gasoline+4 vol. %TBA[1]	A.S.A.[2] 50 ppm	0.8, 1.5
Base gasoline+4 vol. %TBA[1]	A.S.A.+B.H.E.D.[3]	1.3, 1.3
	75 ppm	1.7, 2.2

[1]Tertiary butyl alcohol containing as impurities 5.5 volume per cent acetone; 0.6 volume per cent methanol; 0.5 volume per cent tertiary butyl formate; 1.6 volume per cent water and 50 ppm volume ditertiary butyl peroxide.

[2]An alkenyl succinic anhydride derivative having the formula



[3]Neutral salt formed of 1 part by weight of compound (2) plus 2 parts by weight of a beta-hydroxy ethylene diamine derivative having the formula



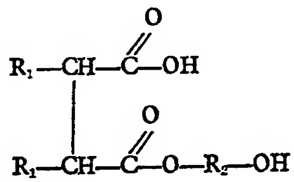
These data show that the preferred inhibitor of this invention is exceedingly effective in preventing corrosion of a metal which is easily corroded and in addition that the preferred carburetor detergents can be used in combination with the corrosion inhibitor and tertiary butyl alcohol.

In addition to these quantitative tests a large number of visual tests were conducted on such metals as copper, zinc and steel. In all of these tests the inhibitor of this invention was found to be ineffective, whereas other commercial inhibitors were found to be ineffective. Moreover, in these visual tests the carburetor detergent set forth above was found to be compatible with the inhibitor and with the tertiary butyl alcohol. In other tests with the gasoline containing the carburetor detergent it was found that it functioned to either remove deposits which had been allowed to accumulate around the throttle plate area of an automotive engine or it prevented deposits from building up in this area when it was used starting with a clean carburetor.

WHAT WE CLAIM IS:—

1. A gasoline motor fuel which contains from 1 to 20 volume per cent of total fuel of tertiary butyl alcohol and from 20 to 100 ppm

by weight based on the total weight of fuel of a corrosion inhibitor having the formula



wherein one R_1 is an alkenyl group having one double bond and from 8 to 16 carbon atoms with the other R_1 being hydrogen and R_2 is a group of the formula

$$—C_nH_{2n}—$$

with n being 2, 3 or 4.

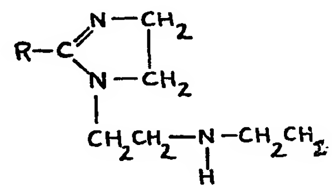
2. A fuel according to claim 1, in which the tertiary butyl alcohol is from 3 to 15 volume per cent of total volume of fuel.

3. A fuel according to either of claims 1 and 2, in which one R_1 is dodecenyl and R_2 is

$$—C_3H_6—.$$

4. A fuel according to any one of claims 1 to 3, in which the fuel also contains a carburetor detergent consisting of a derivative of N-beta-hydroxyethyl ethylene diamine and the combined total of corrosion inhibitor and carburetor detergent is from 20 to 100 ppm by weight based on the total weight of fuel.

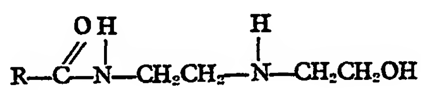
5. A fuel according to claim 4, in which the carburetor detergent has the formula



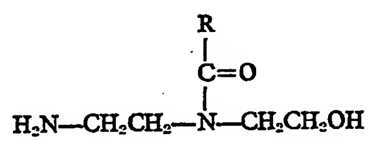
wherein R is alkyl of 12 to 20 carbon atoms or alkenyl with 1 double bond and from 12 to 20 carbon atoms.

6. A fuel according to claim 5, in which R is octadecenyl.

7. A fuel according to claim 4, in which the carburetor detergent is a mixture of two isomeric amides having the respective formulae



and



wherein R is an alkyl radical of from 15 to 19 carbon atoms or alkenyl having from 15 to 19 carbon atoms.

8. A fuel according to claim 7, in which the isomeric amides are produced by the condensation of methyl oleate with N-beta-hydroxyethyl ethylene diamine.

9. A fuel according to any one of claims 4 to 8, in which the weight ratio of the carburetor detergent to the corrosion inhibitor is from 2:1 to 5:1.

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